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(54) Title: FLAME RETARDANT POLYMER BLENDS

(57) Abstract

An antimony-free combination of a phosphate-based flame retardant, especially an aryl diphosphate, and an organoclay afford synergistic flame retardant properties to polymer blends, especially polyphenylene ether-polystyrene blends and blends of polycarbonates with styrene copolymers such as ABS copolymers. The polyphenylene ether-polystyrene blends free from fluorocarbon additives are preferred.

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FLAME RETARDANT POLYMER BLENDS

BACKGROUND OF THE INVENTION

This invention relates to polymer blends, and more particularly to blends having flame retardant properties.

Improvement of the fire resistant properties of polymers has long been a goal of polymer compounders. Fire resistance is typically evaluated by the UL-94 test of Underwriters Laboratories (ASTM procedure D3801). In this test, the desirable V-0 rating is given to polymers of which specimens do not burn with flaming combustion for more than 10 seconds after application of a test flame, and specimens do not burn with flaming combustion for a time exceeding 50 seconds upon 10 flame applications to each of 5 specimens; i.e., the "flame-out time" for said samples is not greater than 50 seconds.

Various types of chemical compounds may be employed as flame retardancy additives. They include halogenated and especially brominated compounds, which often must be used in combination with antimony compounds such as antimony trioxide, and phosphate-based compounds. Such additives are often employed in combination with anti-drip agents such as fluorocarbon polymers.

It is desirable in some instances to employ exclusively phosphate-based compounds. Often, however, very large quantities of such compounds must be present to afford the necessary degree of flame retardancy. Thus, commercial blends of polyphenylene ethers and olefin polymers may require a level of phosphate-based compound above 20 phr (parts by weight per 100 parts of resins). In the case of blends of polycarbonates with alkenylaromatic copolymers (e.g., copolymers of styrene, acrylonitrile and butadiene), a level of phosphate-based compound above 5 phr is typical.

The use of organoclays in combination with flame retardancy additives has been disclosed. For the most part, the additives employed are halogen-based.

US Patent 4,582,866, for example, discloses copolyester elastomers containing as flame retardancy improvers a combination of a bromine compound and antimony trioxide; a clay modified by a quaternary ammonium salt is employed as an anti-drip agent. British Patent 1,114,174 discloses blends of such polymers as polyamides, polystyrenes and olefin polymers with flame retardant additives, which may be halogen- or phosphate-based, and organophilic cation-modified clays as anti-drip agents. According to European patent application 132,228, polyesters may be made flame retardant by the action of a halogenated compound in combination with an antimony or phosphorus compound and an organically modified layered silicate. Similar blends in which the modified clay is used as a "drip suppressant" are disclosed in European patent application 239,986.

Copending, commonly owned application Serial No. 08/950,092 discloses combinations of a polyester, a halogenated flame retardant, an organoclay, an antimony oxide and a fluorocarbon polymer. This combination of additives is described as enabling a decrease in the amounts of halogenated flame retardant and antimony oxide employed.

The aforementioned prior art does not appear to suggest an improved flame retardancy regime applicable to polymer blends. Moreover, it is in no way relevant to the exclusive use of phosphate-based flame retardants and does not point out any possible synergists therefor.

SUMMARY OF THE INVENTION

The present invention is based on the discovery that organoclays may be employed as synergists with phosphate-based flame retardant additives in polymer blends, whereby the levels of

such additives in said blends may be substantially decreased. The function of the organoclay is not simply as an anti-drip agent; it actually forms a synergistic combination with the phosphate-based flame retardant whereby a lower level of the latter may be employed. It has further been found that in certain blends according to the invention, the presence of fluorocarbon polymers is unnecessary and even disadvantageous since such polymers may degrade the flame retardant properties of the blend.

The invention includes compositions free from antimony compounds and comprising the following and any reaction products thereof:

(A) a major amount of a first thermoplastic resin;

(B) a minor amount of at least one second thermoplastic resin, said minor amount being in the range of about 3-45% by weight based on components A and B;

(C) at least one phosphate-based organic compound as the sole flame retardant agent or agents; and

(D) at least one organoclay;

the proportions of components C and D being effective to produce a V-0 rating in the UL-94 test or reduce average flame-out time by at least 10%.

DETAILED DESCRIPTION; PREFERRED EMBODIMENTS

It has not been determined and is immaterial to the invention whether the components of the compositions of the invention undergo chemical interaction to form other materials. Therefore, the invention is directed to said compositions whether or not any chemical interaction has taken place. That is, the invention includes both compositions comprising said components and compositions comprising reaction products thereof.

Components A and B are a first and a second thermoplastic resin. It is intended that said resins differ from each other in structural units. Thus, component A may be a homopolymer and component B a copolymer comprising structural units identical to those of component A in combination with other structural units. Most often, however, components A and B contain totally different structural units.

The chemical structures of the resins constituting components A and B are not critical, subject to the above stipulation. Both addition and condensation polymers are included. Illustrative thermoplastic resins are olefin polymers such as polyethylene and polypropylene; polymers of ethylenically unsaturated carboxylic acids and their functional derivatives, including acrylic polymers such as poly(alkyl acrylates), poly(alkyl methacrylates), polyacrylamides, polyacrylonitrile and polyacrylic acid; alkenylaromatic polymers such as polystyrene; diene polymers such as polybutadiene and polyisoprene; polyamides such as nylon-6 and nylon-66; polyesters such as poly(ethylene terephthalate) and poly(butylene terephthalate); polycarbonates such as bisphenol A polycarbonate; and polyarylene ethers such as poly(2,6-dimethyl-1,4-phenylene ether) and copoly(2,6-dimethyl-1,4-phenylene ether)-(2,3,6-trimethyl-1,4-phenylene ether). Both homopolymers and copolymers are included, and the latter may be of the random, block or graft type. Thus, for example, suitable polystyrenes include homopolymers and copolymers. The latter embraces high impact polystyrene (HIPS), a genus rubber-modified polystyrenes comprising blends and grafts wherein the rubber is a polybutadiene or a rubbery copolymer of about 70-98% styrene and 2-30% diene monomer.

The blend of components A and B may be compatible, incompatible or chemically or physically compatibilized by known methods. It is often preferred that component B be a commercially conventional adjuvant to component A, such as an impact modifier therefor or a second component of a commercial polymer blend.

For many purposes, the preferred polymer blends are those of polyphenylene ethers, especially with homo- and copolystyrenes including homopolystyrene and styrene copolymers with diene rubbers (e.g., high impact polystyrenes), and those of polycarbonates. The polycarbonate blends include those in which component B comprises at least one copolystyrene, especially those in which it comprises one or more styrene copolymers with aliphatic dienes and nitriles (e.g., acrylonitrile -butadiene-styrene or ABS copolymers). The copolystyrenes blended with polycarbonates are frequently mixtures of ABS copolymers and styrene-acrylonitrile copolymers.

Component C may be any one or more phosphate-based organic compound(s) which provide flame retardant properties. By "phosphate-based" is meant an organic compound containing at least one phosphate (PO_4) group.

Suitable phosphate-based compounds include triaryl monophosphates such as tricresyl phosphate. The preferred phosphate-based compounds, however, are the aryl diphosphates. They include compounds of the formula

$$(A^1O)_2P(O)O[A^2OP(O)(OA^1)O]_nA^1,$$

wherein each A^1 is independently a monovalent C_{6-20} aromatic radical, each A^2 is a divalent C_{6-20} aromatic radical and n is 0-5 and preferably 1. Said aromatic radicals may be hydrocarbon or substituted hydrocarbon radicals, with hydrocarbon radicals being preferred. The term "aromatic" embraces monocyclic and polycyclic fused- and linked-ring radicals, including alkylaromatic radicals such as methylphenyl, dimethylphenyl and 2,2-bis(4-phenylene)propane; i.e., the radical derived from bisphenol A.

Examples of suitable aryl diphosphates include hydroquinone bis(diphenyl phosphate), resorcinol bis(diphenyl phosphate), bisphenol A bis(diphenyl phosphate) and resorcinol bis(di-2,6-xylyl phosphate). The preferred diphosphates are generally

resorcinol bis(diphenyl phosphate) and bisphenol A bis(diphenyl phosphate).

Component C is the sole flame retardant agent in the compositions of the invention. Thus, no halogenated flame retardants are present.

Component D is at least one organoclay. As used herein, "organoclay" means a layered clay, usually a silicate clay, derived from a layered mineral and in which organic moieties have been chemically incorporated, ordinarily by ion exchange and especially cation exchange with organic ions and/or onium compounds. Illustrative organic ions are mono- and polyammonium cations such as trimethyldodecylammonium and N,N'-didodecylimidazolium.

Illustrative layered minerals are the kaolinites and the montmorillonites. It is also possible to employ minerals of the illite group, including hydromicas, phengite, brammallite, glaucomite, cejadonite and the like. Often, the preferred layered minerals include those often referred to as 2:1 layered silicate minerals, including muscovite, vermiculite, saponite, hectorite and montmorillonite, the latter often being most preferred. The layered minerals may be synthetically produced, but most often they are naturally occurring and commercially available. A detailed description of suitable layered minerals can be found in US Patent 5,530,052, the disclosure of which is incorporated by reference herein.

Suitable specific commercially available or easily prepared organoclays which are illustrative of those which may be employed include CLAYTONE HY, a montmorillonite cation exchanged with dimethyldi(hydrogenated tallow)ammonium ion available from Southern Clay Products, and montmorillonite cation exchanged with such ions as dodecylammonium, trimethyldodecylammonium, N,N'-didodecylimidazolium, N,N'-ditetradecylbenzimidazolium or methylbis(hydroxyethyl)-(hydrogenated tallow)ammonium.

The compositions of this invention may contain conventional additives for polymer blends of these types, with the proviso that no antimony compounds are employed as additives. Suitable additives include anti-drip agents, stabilizers, fillers, pigments, dyes, antistatic agents, crystallization aids and mold release agents. Since these are well known in the art, they will not be dealt with in detail herein.

It is often preferred in compositions in which component A is a polyphenylene ether, and especially where component B is a polymer of one or more ethylenically unsaturated monomers and component C is present at relatively low levels, that fluorocarbon polymers not be employed as anti-drip agents. A preferred embodiment of the invention, therefore, is polyphenylene ether blends wherein the level of component C is less than 20 parts by weight per 100 parts of the combination of components A and B (phr), said blends being free from fluorocarbon polymers. The presence of such polymers in these blends may result in degradation of flame retardant properties, as exemplified by UL-94 rating, flame-out time or both.

The proportions of components in the compositions of the invention are subject to wide variation. Component A is present in major amount with respect to the combination of components A and B, with component B comprising about 3-45% and preferably about 5-40% by weight of said combination.

Components C and D are present in amounts effective to produce a V-0 rating in the UL-94 test or reduce average flame-out time by at least 10%. This amount will vary with the identities of components A and B.

When component A is a polyphenylene ether, and especially when component B is an addition polymer of one or more ethylenically unsaturated monomers, the proportion of component C is most often in the range of 10-25 and preferably 15-20 phr. At levels higher than 20 phr, it is frequently unnecessary to employ component D to obtain acceptable flame retardancy; below 15 phr, it may be

impossible to provide the desired balance of flame retardancy and other properties even with the use of components C and D.

In polycarbonate blends, especially with addition polymers of ethylenically unsaturated monomers, the proportion of component C is typically in the range of about 5-15 and preferably 7-11 phr. Lower levels may afford little or no flame retardancy even in the presence of component D, and higher levels are unnecessary and may minimize the effect of component D.

It is generally advantageous to employ component D in the amount of 0.08-0.6 phr, with higher levels affording no advantage and even sometimes decreasing flame retardancy and/or degrading any polycarbonate present in the blend. Even within this range some variability of effectiveness is noted, particularly at borderline levels of component C. Those skilled in the art can, however, easily determine effective levels via simple experimentation.

In blends in which a fluorocarbon polymer, most often polytetrafluoroethylene (PTFE), is employed as an anti-drip agent, it is generally employed in the range of about 0.1-0.5 phr.

The compositions of this invention may be prepared by conventional blending techniques for thermoplastic resins. These may include solution blending and melt blending. Melt blending, especially by methods suitable for continuous operation such as extrusion, is often preferred.

The invention is illustrated by the following examples. All parts and percentages are by weight. Molecular weights are weight average and were determined by gel permeation chromatography. Intrinsic viscosities were determined in chloroform at 25 °C. UL-94 tests were conducted on 1/16" (1.6 mm) specimens.

EXAMPLE 1

A series of experiments was conducted on blends of 64.32 parts of a poly(2,6-dimethyl-1,4-phenylene ether) having an

intrinsic viscosity of 0.46 dl/g; 35.68 parts of a HIPS having a molecular weight in the range of 210,000-250,000, a rubber content of 10.3% and a melt flow index of 2.2-3.1 g/10 min; 5.49 phr of conventional additives including stabilizers, impact modifiers and mold release agents; 0.15 phr of a blend of 50% poly(tetrafluoroethylene) and 50% of a styrene-acrylonitrile copolymer comprising 72% styrene units("PTFE blend"); and various proportions of resorcinol bis(diphenyl phosphate) including 5.32, 10.63, 15.95 and 21.26 phr. The blends were prepared by mixing the constituents in a Henschel mixer and extruding at temperatures in the range of 120-232 °C on a 20-mm twin screw extruder with counterrotating screws. It was found that 21.26 phr of the diphosphate was required to produce a V-0 rating in the UL-94 test.

Similar blends containing 21.26 phr of the diphosphate were prepared, both containing and not containing the PTFE and CLAYTONE HY organoclay. UL-94 test results and average flame-out times for 5 sets of 5 test specimens each (FOT) were determined and the results are listed in TABLE I.

TABLE I

Entry	1	2	3	4
Organoclay, phr	0	0	0.50	0.50
PTFE blend, phr	0.15	0	0.15	0
UL-94 rating	V-0	V-0	V-0	V-0
FOT, sec	22.0	28.9	23.3	21.2
FOT % decrease	--	--	--	26.6

It is apparent from a comparison of entries 2 and 4 with entries 1 and 3 that at this level of diphosphate, the presence of PTFE blend produces an improvement in FOT. The presence of organoclay

has no detrimental effect in the presence of PTFE (entries 2 and 4) and has a beneficial effect when PTFE is absent (entries 1 and 3).

EXAMPLE 2

Blends similar to those of Example 1, but containing 15.95 phr of diphosphate, were prepared and tested. The results are given in TABLE II.

TABLE II

Entry	5	6	7	8
Organoclay, phr	0	0	0.50	0.50
PTFE blend, phr	0.15	0	0.15	0
UL-94 rating	V-1	V-0/V-1	V-1	V-0
FOT, sec	40.9	35.3	35.8	29.6
FOT % decrease	--	--	12.5	16.1

At this level of diphosphate (below 20 phr), the presence of PTFE causes a degradation of the flame retardant properties of the blend. This can be seen by comparing Entries 5 and 7 with Entries 6 and 8. The presence of organoclay produces a substantial decrease in FOT, independent of the presence or absence of PTFE (Entries 7-8 vs. entries 5-6).

EXAMPLE 3

Blends similar to those of Example 1 but containing bisphenol A bis(diphenyl phosphate) in the amount of 25.80 phr were prepared and evaluated. The results are given in TABLE III.

TABLE III

Entry	9	10	11	12
Organoclay, phr	0	0	0.50	0.50
PTFE blend, phr	0	0.14	0	0.14
UL-94 rating	V-0	V-0	V-0	V-0
FOT, sec	38.25	40.5	29.5	31.25
FOT % decrease	--	--	22.9	22.8

Again, the benefit provided by the presence of organoclay is apparent. No substantial effect on flame retardant properties as a result of the presence of PTFE is apparent.

EXAMPLE 4

Blends identical to those of Example 3 but containing 19.35 phr of bisphenol A bis(diphenyl phosphate) were prepared and tested. The results are given in TABLE IV.

TABLE IV

Entry	13	14	15	16
Organoclay, phr	0	0	0.50	0.50
PTFE blend, phr	0	0.14	0	0.14
UL-94 rating	V-0	V-1	V-0	V-1
FOT, sec	40.8	57.9	32.6	54.0
FOT % decrease	--	--	20.1	6.7

Again, it is apparent that the presence of organoclay results in an improvement in flame retardant properties and that the presence of PTFE degrades those properties at this level of diphosphate.

EXAMPLE 5

The blending procedure of Example 1 was employed to prepare blends comprising about 81.7% of a linear bisphenol A polycarbonate resin having an intrinsic viscosity of 0.50 dl/g; about 18.3% of a mixture of the following addition copolymers: (1) 45.5% of a commercially available emulsion polymerized ABS graft copolymer comprising a discontinuous elastomeric phase (polybutadiene with an average particle size of about 300 nm) and a rigid thermoplastic phase (copolymer of 75 pbw styrene and 25 pbw acrylonitrile) and (2) 54.5% of a styrene-acrylonitrile copolymer (SAN, 75 parts styrene/25 parts acrylonitrile) having a molecular weight of about 90,000; 9.5 phr of resorcinol bis(diphenyl phosphate); and 0.4 phr of PTFE blend. There were immaterial differences in the proportions of polycarbonate and addition polymers in these blends, but those differences are not believed to have had any effect on the properties studied. The results are given in TABLE V.

TABLE V

Entry	17	18	19	20
Organoclay, phr	0	0.1	0.25	0.50
UL-94 rating	V-0	V-0	V-0	V-0
FOT, sec	27.5	22.25	31	36.75
FOT % decrease	--	19.0	--	--

The results in TABLE V show that at this level of diphosphate, only 0.1 phr of organoclay affords an improvement in flame retardant properties.

EXAMPLE 6

Blends similar to those of Example 5 but comprising about 82% polycarbonate, 18% addition polymers and 7.5 phr diphosphate were prepared and tested. The results are given in TABLE VI.

TABLE VI

Entry	17	18	19	20
Organoclay, phr	0	0.1	0.25	0.50
UL-94 rating	V-1	V-1	V-1	V-1
FOT, sec	69.75	61	40.25	65.75
FOT % decrease	--	12.5	42.3	5.7

At this level of diphosphate, organoclay proportions from 0.1 to 0.25 phr afforded the desired improvement in flame retardant properties.

EXAMPLE 7

Blends similar to those of Example 5 but comprising about 82.4% polycarbonate, 17.6% addition polymers and 6.0 phr diphosphate were prepared and tested. The results are given in TABLE VI.

TABLE VI

Entry	21	22	23	24
Organoclay, phr	0	0.1	0.25	0.50
UL-94 rating	V-1	V-1	V-1	V-1
FOT, sec	84.5	86.5	157.25	152.5
FOT % decrease	--	--	--	--

At this level of diphosphate, no amount of organoclay produced an improvement in flame retardant properties.

What is claimed is:

1. A composition free from antimony compounds and comprising the following and any reaction products thereof:

(A) a major amount of a first thermoplastic resin;

(B) a minor amount of a second thermoplastic resin, said minor amount being in the range of about 3-45% by weight based on components A and B;

(C) at least one phosphate-based organic compound as the sole flame retardant agent or agents; and

(D) at least one organoclay;

the proportions of components C and D being effective to produce a V-0 rating in the UL-94 test or reduce average flame-out time by at least 10%.

2. A composition according to claim 1 wherein component C is at least one aryl diphosphate.

3. A composition according to claim 2 wherein the proportion of component B is about 5-40% of the combination of components A and B.

4. A composition according to claim 2 wherein the amount of component D is in the range of 0.08-0.6 parts by weight per 100 parts of the combination of components A and B. (claim deleted)

5. A composition according to claim 4 wherein component C is resorcinol bis(diphenyl phosphate).

6. A composition according to claim 4 wherein component C is bisphenol A bis(diphenyl phosphate).

7. A composition according to claim 4 wherein component D is a montmorillonite in which organic moieties have been incorporated by cation exchange.

8. A composition according to claim 4 wherein component A is a polyphenylene ether.

9. A composition according to claim 8 wherein component A is a poly(2,6-dimethyl-1,4-phenylene ether).

10. A composition according to claim 8 wherein the amount of component C is an amount less than 20 parts by weight per 100 parts of the combination of components A and B.

11. A composition according to claim 10 which is free from fluorocarbon polymers.

12. A composition according to claim 11 wherein component B is a polymer of one or more ethylenically unsaturated monomers.

13. A composition according to claim 12 wherein component B is a homo- or copolystyrene.

14. A composition according to claim 13 wherein component B is a high impact polystyrene.

15. A composition according to claim 2 wherein component A is a polycarbonate.

16. A composition according to claim 15 wherein component A is a bisphenol A polycarbonate.

17. A composition according to claim 15 further comprising an anti-drip amount of at least one fluorocarbon polymer.

18. A composition according to claim 17 wherein component B comprises at least one ABS copolymer.

19. A composition according to claim 18 wherein component B is a mixture of at least one ABS copolymer and at least one styrene-acrylonitrile copolymer.

INTERNATIONAL SEARCH REPORT

Inte onal Application No
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A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08K5/523 C08L69/00 C08L71/12 C08K9/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
E	EP 0 899 301 A (GEN. ELECTRIC) 3 March 1999 see page 4, paragraph 20 - page 5, paragraph 21 see page 5, paragraph 25; claims 1,7	1,7
A	WO 93 04119 A (GEN. ELECTRIC) 4 March 1993 see examples	1,2,8,9,13
A	EP 0 736 490 A (GEN. ELECTRIC) 9 October 1996 see page 2, paragraph 2; claims 1,14-19; example 8	1,7-9

[ ] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
1 June 1999	14/06/1999

Name and mailing address of the ISA	Authorized officer
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